

Cadmium(II) and calcium(II) complexes with *N,O*-bidentate ligands derived from pyrazinecarboxylic acid

Thermal data and crystal structure correlation

Barbara Barszcz · Joanna Masternak ·
Maciej Hodorowicz · Agnieszka Jabłońska-Wawrzyska

ICVMTT2011 Conference Special Chapter

© The Author(s) 2012. This article is published with open access at Springerlink.com

Abstract The synthesis and characterization of cadmium(II) and calcium(II) complexes with *N,O*-bidentate ligands derived from pyrazinecarboxylic acid (3-hydroxy-2-quinoxalinecarboxylic acid HL^1 , pyrazine-2-carboxylic acid HL^2) are reported. Obtained compounds $[Cd(L^1)_2(H_2O)_2](H_2O)_2$ (**1**), $[Cd(L^2)_2]_n$ (**2**) and $[Ca(L^2)_2(H_2O)_4]$ (**3**) were studied by elemental analyses, IR, Raman spectroscopy and thermogravimetric methods (TG, DTG, DSC). In addition, the molecular structure of complex **1** has been determined by X-ray single crystal diffraction. Thermal analysis reveals a decomposition process of **1**, **3** complexes in multiple stages. The data obtained from TG and DSC curves for **1**, **3** confirm not only the presence but also the nature of water (crystallization and coordination) and the stoichiometry of the studied metal complexes. The results of thermal studies are in good agreement with their crystal structures. Thermal behavior of complex **2** indicates a single complete decomposition process of the sample. In addition, complex **2** as a coordination polymer is the most stable all of them and the thermal stability of the obtained complexes can be ordered in the following sequence: $1 < 3 \ll 2$.

Keywords Cadmium(II) and calcium(II) complexes · 3-Oxo-4H-quinoxaline-2-carboxylate · Pyrazine-2-carboxylate · Crystal structure · TG/DTG · DSC analysis

Introduction

Recently, our research group has embarked on a comparative study of coordination chemistry of calcium and cadmium model complexes with *N,O*-biologically important ligands to find differences and similarities related to their thermal stability and molecular structures [1, 2]. The similarities presented by Ca(II) and Cd(II) ions (they show similarity in their radius 0,95 and 1,00 Å) favor the exchange of the metals in the biological system. Therefore, a comparison of coordination chemistry of calcium and cadmium model complexes ought to provide a solid-based example of how toxic metal ion substitution may perturb the structure of the calcium compound with the same or derivative ligand. As an extension of this study, we report here the synthesis, spectroscopic analysis, X-ray crystallography and thermal behavior of cadmium(II) complex with 3-hydroxy-2-quinoxalinecarboxylate (L^1). We have not found the crystal structure of $[Cd(L^1)_2(H_2O)_2](H_2O)_2$ in the literature. Furthermore, the study included the comparison of spectroscopic data and thermal stability of Cd(II) (**2**) and Ca(II) (**3**) complexes with pyrazine-2-carboxylate. Compounds **2** and **3** were first reported by Liu [3] and Ptasiwicz-Bąk with coworkers [4], respectively. Liu [3] synthesized $[Cd(L^2)_2]_n$ in a hydrothermal method using cadmium(II) nitrate, pyrazine-2-carboxylate, NaOH, and water (20% yield). Complex **3** was isolated from the reaction of pyrazine-2-carboxylic acid (HL^2) and calcium oxide.

In this article, we report an alternative, non-hydrothermal preparation which has afforded **2** and **3** in high yield. Bearing in mind that the coordination ability of the carboxylate ligands toward metal ions frequently depends on hydrothermal or non-hydrothermal methods used to prepare the complexes [1, 5–8], we investigated the crystal structure of obtained compounds with X-ray crystallography. By

B. Barszcz (✉) · J. Masternak · A. Jabłońska-Wawrzyska
Institute of Chemistry, The Jan Kochanowski University
of Humanities and Science, 15G Świętokrzyska Str.,
25-406 Kielce, Poland
e-mail: Barbara.Barszcz@ujk.kielce.pl

M. Hodorowicz
Faculty of Chemistry, Jagiellonian University, 3 Ingardena Str.,
30-060 Kraków, Poland

comparing the crystallographic data, it can be seen that the crystal structure of the obtained complexes look similar to those reported in the literature [3, 4]. However, up to now, the spectroscopic data (IR, Raman) and thermal properties of the two complexes have not been found in the literature.

Both of the ligands have a recognized biological function in the body metabolism. 3-hydroxy-2-quinoxalinecarboxylic acid (HL^1) was found to antagonize the $^{22}Na^+$ efflux produced in $^{22}Na^+$ -preloaded brain slices by *N*-methyl-D-aspartate and kainate [9]. Pyrazine-2-carboxylic acid (HL^2) is the active form which is encoded by the *pncA* gene for activity against *Mycobacterium tuberculosis* [10]. In addition, the in vitro antibacterial screening of the free acid and its metal complexes has been carried out against *Escherichia coli*, *Salmonella typhi* and *Vibrio cholera* [11]. Moreover, carboxylates [12–14] are versatile ligands which offer a great variety of coordination modes (Scheme 1) and this makes them interesting in the construction of molecular architectures.

Experimental procedure

Reagents and physical measurement

All reagents (pyrazine-2-carboxylic acid, 3-hydroxy-2-quinoxalinecarboxylic acid, the metal salts) were purchased from Aldrich, Merck Chemical and used as received. Ethanol was purchased from Linegal Chemicals and water was deionised.

Elemental analyses (C, N, H) were performed on Model 240 Perkin-Elmer CHN Analyzer. Elemental analysis of Cd^{2+} was carried out using ICP-MS method (ELAN DRCII, PerkinElmer). A sample of the compound was dissolved in a solution of 2% HNO_3 and diluted. Calibration solution available from PerkinElmer (1000 mg L^{-1} , 2% HNO_3 [7440-43-9]). ESI-MS spectra was carried out with a micrOTOF-QII instrument (Bruker). IR spectra were recorded with Nicolet 380 FTIR spectrophotometer in the region 4000–400 cm^{-1} using the diffusive reflection method. Fourier transforms Raman scattering measurements (FT-RS) were performed at room temperature with a PerkinElmer RamanStation™ 400F spectrometer, resolution 4 cm^{-1} . The incident radiation

($\lambda = 785$ nm) came from a diode laser. The thermal decompositions of ~ 10 mg of the prepared complexes were measured under the static air atmosphere with Mettler-Toledo Star TG/SDTA 851^c thermal analyzer at a heating rate of 5 $K min^{-1}$. For all complexes in the temperature range of 298–1273 K alumina open crucibles were used. DSC analysis was carried out using DSC Mettler-Toledo instrument in standard closed sample pans, static air atmosphere, and heating rate of 5 $K min^{-1}$. The thermoanalytical curves were obtained using STAR^c System METTLER-TOLEDO software. The powder X-ray diffraction (XRD) patterns of the products of decomposition were recorded by DRON-2 using CuK_{α} radiation ($\lambda = 1.54178$ Å) over 2θ angle range 8–65°.

Syntheses of the complexes

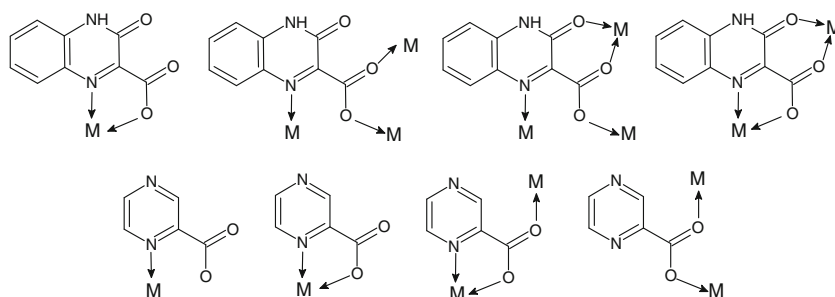
Preparation of $[Cd(L^1)_2(H_2O)_2](H_2O)_2$ (1)

A solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.5 mmol) in deionised water (5 mL) was slowly added to a solution of 3-hydroxy-2-quinoxalinecarboxylic acid (HL^1) (1 mmol), in ethanol (15 mL). The molar ratio M:L was 1:2. The mixture was heated (~ 323 K) and stirred for 7 h, then left standing at room temperature. Passive evaporation of green solution resulted in yellow crystals of the complex suitable for X-ray investigation. The product was filtered and dried under vacuum. The crystals were collected in 45% yield. Anal. Calc. for $C_{18}H_{18}N_4O_{10}Cd$: C, 38.40, N, 9.98, H, 3.00, Cd, 19.96. Found: C, 38.42, N, 9.96, H, 3.22, Cd, 19.98%. ESI-MS (positive ion mode, acetonitrile): m/z (%) $[Cd(L^1)_2(CH_3CN)_2]Na^+ = 613$ (100), $[Cd(L^1)_2(H_2O)_2]Na^+ = 551$ (40), $[Cd(L^1)_2(H_2O)_2](H_2O)_2H^+ = 565$ (30), $[Cd(L^1)_2(H_2O)_2](H_2O)_2 K^+ = 603$ (25). The complex was readily soluble in dimethylformamide.

Preparation of $[Cd(L^2)_2]_n$ (2) and $[Ca(L^2)_2(H_2O)_4]$ (3)

The Cd(II) and Ca(II) crystals of complexes with pyrazine-2-carboxylate (L^2) suitable for X-ray investigation and thermal analyses were prepared according to the following procedure: a solution of pyrazine-2-carboxylic acid (HL^2) (2 mmol) in redistilled water (15 mL) heated to 343 K was stirred, while $CaCO_3$ or $Cd(NO_3)_2 \cdot 4H_2O$ (1 mmol) in

Scheme 1 Possible coordination modes of the 3-oxo-4H-quinoxaline-2-carboxylate and pyrazine-2-carboxylate



40 mL redistilled water was added drop wise to the solution. After 3 h, the resulting mixture was cooled to room temperature. The solution was filtered to remove any undissolved material and left to crystallize at room temperature. After 3 days, the colorless crystals were collected by vacuum filtration, washed with mother liquid and dried in a vacuum box. The products were collected in 53 and 86% yield, respectively. *Anal.* Calc. for: $C_{10}H_6N_4O_4Cd$: C, 33.49, N, 15.62, H, 1.69. Found: C, 33.50, N, 15.75, H, 1.64%. *Anal.* Calc. for: $C_{10}H_{14}N_4O_8Ca$: C, 33.52, N, 15.64, H, 3.94. Found: C, 33.59, N, 15.62, H, 3.95%. The complexes were insoluble in most polar and non-polar solvents.

Crystal structure determination

Diffraction intensity data for single crystal of new cadmium complex were collected at room temperature on a KappaCCD (Nonius) diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). Corrections for Lorentz, polarization and absorption effects [15, 16] were applied. The structure was solved by direct methods using SIR-92 program package [17] and refined using a full-matrix least square procedure on F^2 using SHELIXL-97 [18]. Anisotropic displacement parameters for all non-hydrogen atoms and isotropic temperature factors for hydrogen atoms were introduced. In the structure the hydrogen atoms connected to carbon atoms were included in calculated positions from the geometry of molecules, whereas hydrogen atoms of water molecules were included from the difference maps and were refined with isotropic thermal parameters. Further details of the structure analysis are given in Table 1. The figures were made using DIAMOND software [19]. CCDC 830735 contains the supplementary crystallographic data for complex 1. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic data Centre (CCDC), 12 Union Road, Cambridge CB2 1 EZ, UK; fax: (+44) 1223 366 033; email: deposit@ccdc.cam.ac.uk.

Results and discussion

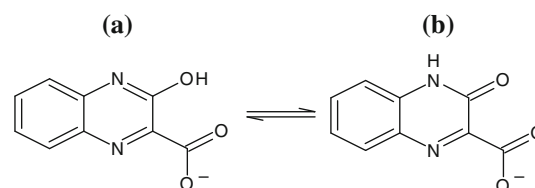
3-Hydroxy-2-quinoxalinecarboxylate due to the labile hydrogen atom of OH-group in α -position to the basic pyrimidine N atom forms enol-keto tautomers (Scheme 2).

The molecular and crystal structure of cadmium complex $[Cd(L^1)_2(H_2O)_2](H_2O)_2$ (**1**)

The asymmetric unit of title compound, $[Cd(C_9H_5N_2O_3)_2(H_2O)_2](H_2O)_2$, consists of octahedrally coordinated Cd^{2+} ions, with the 3-oxo-3,4-dihydroquinoxaline-2-carboxylate

Table 1 Crystal data and structure refinement for **1**

	$[Cd(L^1)_2(H_2O)_2](H_2O)_2$
Empirical formula	$Cd C_{18} H_{18} N_4 O_{10}$
Formula weight	562.63
T/K	293(2)
Wavelength/Å	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimension	
$a/\text{Å} = 6.8300(4)$	$\alpha/^\circ = 76.229(4)$
$b/\text{Å} = 8.0310(4)$	$\beta/^\circ = 76.450(3)$
$c/\text{Å} = 9.6620(5)$	$\gamma/^\circ = 77.480(4)$
$V/\text{Å}^3$	493.09(5)
$Z, D_{\text{calc}}/\text{mg m}^{-3}$	1, 1.895
Absorption coefficient/ mm^{-1}	1.177
$F(000)$	282
Crystal size/mm	$0.19 \times 0.13 \times 10$
$\theta/^\circ$	2.65–27.38
Index ranges	$-8 \leq h \leq 8, -10 \leq k \leq 10, -11 \leq l \leq 12$
Reflections collected/unique	6,872/2,155 [$R_{\text{int}} = 0.0582$]
Max. and min. transmission	0.8914 and 0.8074
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2216/6/167
Goodness-of-fit (GOF) on F^2	1.077
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0290, wR_2 = 0.0726$
R indices (all data)	$R_1 = 0.0304, wR_2 = 0.0733$
Extinction coefficient	0.023(4)
Largest differences in peak and hole/ $e\text{Å}^{-3}$	0.455 and -0.879



Scheme 2 Enol **a** keto **b** tautomers of 3-hydroxy-2-quinoxaline-carboxylate

ligands acting in a bidentate manner ($Cd-O(1) = 2.2644(16)$ Å and $Cd-N(1) = 2.3513(18)$ Å), a water molecule coordinated axially (apical) via the O(4) atom ($Cd-O(4) = 2.3219(19)$ Å) and additional water of crystallization molecule. The Diamond drawing of the $Cd(II)$ complex with atom numbering is shown in Fig. 1. Selected geometrical data for the compound are given in Table 1. On the basis of the observed valence angles (Table 2) the shape of coordination polyhedron can be described as distorted octahedron $\{CdO_4N_2\}$. The octahedron around the Cd^{2+} atom, which lies on an inversion center, is slightly flattened in the equatorial direction. The ligand exhibits

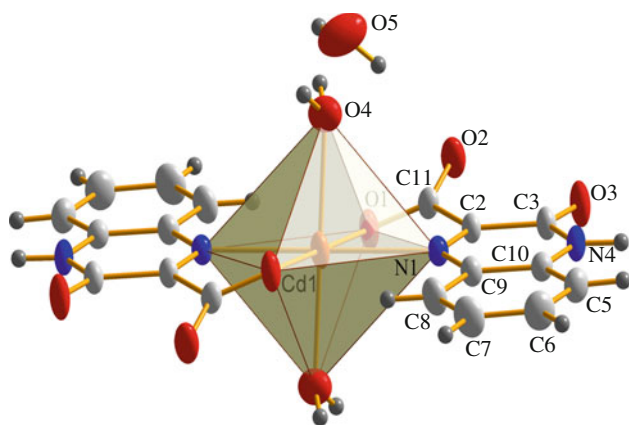


Fig. 1 Molecular structure of $[\text{Cd}(\text{L}^1)_2(\text{H}_2\text{O})_2](\text{H}_2\text{O})_2$ (**1**) mono

Table 2 Selected bond lengths/Å and valence angles/° for **1**

Bond lengths/Å		Valence angles/°	
Cd–O(1) ⁱ	2.2644(16)	O(1) ⁱ –Cd–O(1)	180.00
Cd–O(1)	2.2644(16)	O(1) ⁱ –Cd–O(4)	95.91(7)
Cd–O(4)	2.3219(19)	O(1)–Cd–O(4)	84.09(7)
Cd–O(4) ⁱ	2.3219(19)	O(1) ⁱ –Cd–O(4) ⁱ	84.09(7)
Cd–N(1) ⁱ	2.3513(18)	O(1)–Cd–O(4) ⁱ	95.91(7)
Cd–N(1)	2.3513(18)	O(1)–Cd–O(4) ⁱ	180.0
		O(1) ⁱ –Cd–N(1) ⁱ	71.36(6)
		O(1)–Cd–N(1) ⁱ	108.64(6)
		O(1)–Cd–N(1) ⁱ	92.76(7)
		O(1) ⁱ –Cd–N(1) ⁱ	87.24(7)
		O(1) ⁱ –Cd–N(1)	108.64(6)
		O(1)–Cd–N(1)	71.36(6)
		O(4)–Cd–N(1)	87.24(7)
		O(4) ⁱ –Cd–N(1)	92.76(7)
		N(1) ⁱ –Cd–N(1)	180.0

Symmetry transformations used to generate equivalent atoms:
(i) $-x + 1, -y, -z + 1$

enol-to-keto tautomerization by H-atom transfer from the hydroxyl group at position 3 to the N atom at position 4 of the quinoxaline ring of the ligand. The chelate ring defined by atoms Cd(1)/O(1)/C(11)/C(2)/N(1) is approximately planar, with a maximum out-of-plane deviation of 0.116 Å for Cd. This plane makes a small angle of 3.69(13) with the planar quinoxaline ring (atoms N(1)/C(2)/C(3)/N(4)/C(10)/C(9)). The geometry of the quinoxaline ring corresponds to tautomeric protonation at N(4) ($\text{O}(3)\text{--C}(3) = 1.226(3)$ Å and $\text{C}(3)\text{--N}(4) = 1.363(3)$ Å) [20]. The $\text{O}(1)\text{--C}(11)$ bond distance of the carboxylate group (1.254(3) Å) is longer than $\text{O}(2)\text{--C}(11)$ (1.240(3) Å), due to the coordination of atom O(1) to Cd^{2+} . Packing analysis reveals that the complex has a very interesting coordination network

(Fig. 2). The complex molecules are linked through an intermolecular $\text{N--H}\cdots\text{O}$ hydrogen bond ($\text{N}(4)\cdots\text{O}(3) = 2.804(3)$ Å) formed between the quinoxaline NH group and a carbonyl O atom, and by five $\text{O--H}\cdots\text{O}$ hydrogen bonds formed between a O atoms of ligand and water molecules (Table 3). In addition, there is a intermolecular $\text{O--H}\cdots\text{O}$ hydrogen bond (2.819(3) Å) formed between a two water molecules (Table 3).

Infrared and Raman spectra

The most important IR (Raman) frequencies attributed to the vibrations of free acids and complexes **1–3** are reported in Table 4. The IR spectrum of both free acids, 3-hydroxy-2-quinoxalinecarboxylic acid (HL^1) and pyrazine-2-carboxylic acid (HL^2) show a strong band centered at 1755 cm^{-1} (1763) and 1714 cm^{-1} (1709), respectively assigned to stretching vibration of the non-ionized carboxyl groups which are absent in the spectrum of the complexes, confirming that the carboxylic groups are deprotonated. Furthermore, the infrared spectrum of $[\text{Cd}(\text{L}^1)_2(\text{H}_2\text{O})_2](\text{H}_2\text{O})_2$ display an intense stretch at 1678 (1685 cm^{-1}) corresponding to $\nu(\text{C=O})_{\text{ketone}}$ stretching vibration [21] and the in-plane $\delta(\text{NH})$ band (at: 1616 cm^{-1}) suggesting the protonation of pyrazine nitrogen atom, and indicates the coordination of keto tautomers, 3-oxo-4H-quinoxaline-2-carboxylate (L^1) to $\text{Cd}(\text{II})$ ion. This is in agreement with the results of the X-ray analysis (Fig. 1). The new broad absorption band of medium intensity in the spectra in the region $3000\text{--}3500\text{ cm}^{-1}$ of **1** and **3** indicates hydrogen bonds involving water molecules coordinated to metals ions or molecules of lattice water. In addition, infrared spectroscopy confirms a bidentate fashion of coordination of L^1 and L^2 ligands to the metal ion via the carboxylate group and nitrogen atom from the pyrazine ring (Table 4). The calculated values of $\Delta(\nu_{\text{asym}}(-\text{COO}^-)) - (\nu_{\text{sym}}(-\text{COO}^-))$ for **1** (276 (275)), **2** (313, 328 (294)), and **3** (238 (231)) indicate the presence of carboxylate groups coordinated to metal ions in unidentate mode [22, 23], which is in agreement with the crystal structures of **1**, **2**, and **3**. Moreover, the IR data confirm that the carboxylate of the ligand **2**, adopts two types of coordination modes: bridging and unidentate.

Thermal analysis and structure correlation

Plausible tentative thermal degradation patterns proposed for the metal complexes under air are presented in Fig. 3. The thermal data of three compounds are collected in Table 5 and the result concerning thermal decomposition are presented as follows:

Fig. 2 Crystal packing of cadmium(II) complex (**1**) showing the water molecules placement (view [1 0 0])

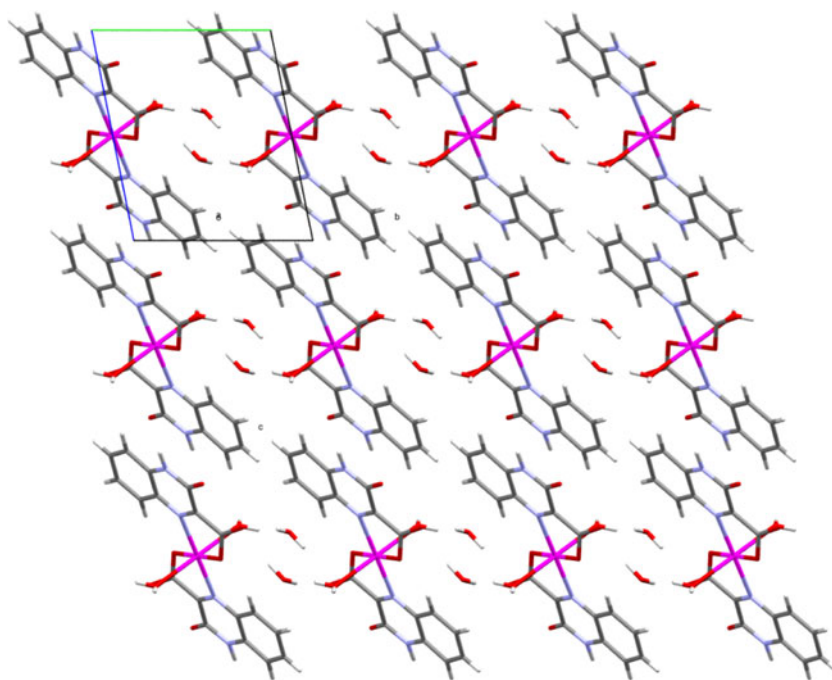


Table 3 Hydrogen bonds lengths/Å and valence angles/° for **1**

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(4)–H(4A)···O(2) ⁱ	0.861(19)	2.02(3)	2.842(3)	158(5)
O(4)–H(4A)···O(3) ⁱ	0.861(19)	2.50(4)	3.004(3)	118(4)
O(4)–H(4B)···O(5)	0.900(19)	1.96(3)	2.819(3)	158(5)
O(5)–H(5A)···O(2)	0.904(19)	2.18(2)	3.074(3)	168(5)
O(5)–H(5B)···O(2) ⁱⁱ	0.904(19)	2.07(2)	2.966(3)	171(5)
N(4)–H(4)···O(3) ⁱⁱⁱ	0.89(5)	1.91(5)	2.804(3)	174(4)

Symmetry transformations used to generate equivalent atoms: (i) $x + 1, y, z$; (ii) $-x, -y + 1, -z + 1$; (iii) $-x, -y, -z$

Table 4 The most characteristic bands in the IR (Raman) spectra for 3-hydroxy-2-quinoxalinecarboxylic acid (HL¹), pyrazine-2-carboxylic acid (HL²), and its complexes/cm^{−1}

Assignments	HL ¹	[Cd(L ¹) ₂ (H ₂ O) ₂](H ₂ O) ₂	HL ²	[Cd(L ²) ₂] _n	[Ca(L ²) ₂ (H ₂ O) ₄]
$\nu(\text{OH}_{\text{H}_2\text{O}})$	–	3364 <i>vb</i>	–	–	3400–3100 <i>vb</i>
$\nu(\text{O} \cdots \text{HN})$	3138–2950 <i>vb</i>	3000–2800 <i>vb</i>	–	–	–
$\nu(\text{COOH})$	1755 (1763)	–	1714 (1709)	–	–
$\nu_{\text{as}}, \nu_{\text{s}}(\text{COO}^-)$	–	1648, 1372 $\Delta = 276$ (1660, 1385 $\Delta = 275$)	–	1613, 1300; 1285 $\Delta = 313, 328$ (1581; 1287 $\Delta = 294$)	1610, 1372 $\Delta = 238$ (1613, 1382 $\Delta = 231$)
Pyrazine ring vibration	1596, 1493, 1417 (1593, 1420)	1587, 1492, 1398 (1584, 1400)	1571, 1484, 1394 (1591, 1396)	1573, 1470, 1408 (1472, 1410, 1574)	1577, 1472, 1414 (1581, 1474, 1414)
$\nu(\text{C}=\text{O})_{\text{ketone}}$	1684 (1690)	1678 (1685)	–	–	–
$\delta(\text{C}=\text{O})$	1053 (1100)	1046 (1109)	1049 (1054)	1040 (1044)	1049 (1058)
δNH	1608 (1606)	1604 (1601)	–	–	–

vb very broad

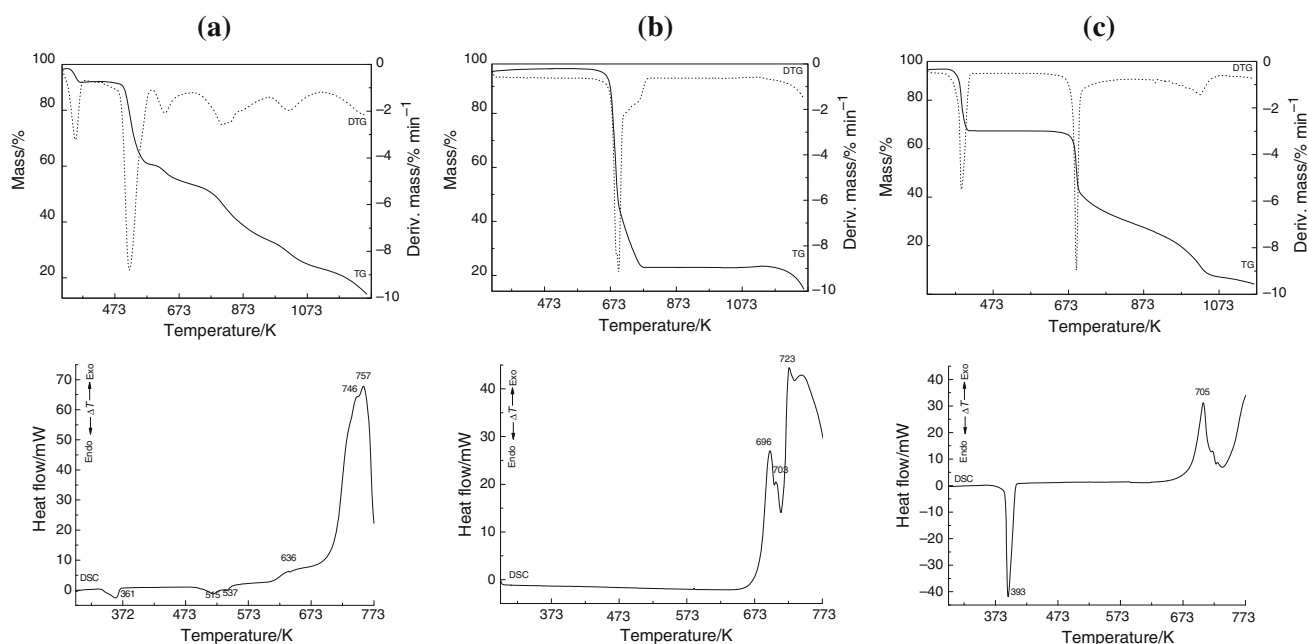


Fig. 3 Thermoanalytical curves (TG/DTG and DSC) of the compounds $[\text{Cd}(\text{L}^1)_2(\text{H}_2\text{O})_2](\text{H}_2\text{O})_2$ (a), $[\text{Cd}(\text{L}^2)_2]_n$ (b), $[\text{Ca}(\text{L}^2)_2(\text{H}_2\text{O})_4]$ (c)

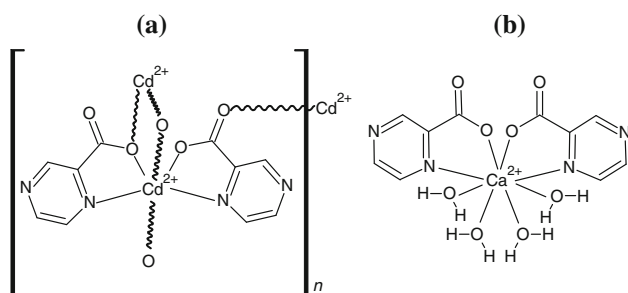
Table 5 Thermoanalytical results (TG/DTG, DSC) of cadmium(II) and calcium(II) complexes

Complex	Stage	TG results	DTG (DSC) results	Peak nature	Mass/%		Loss	Residue
		$T_{\text{range}}/\text{K}$	$T_{\text{max. peaks}}/\text{K}$		Calc.	Found		
[Cd(L ¹) ₂ (H ₂ O) ₂](H ₂ O) ₂	I	333–383	350 (361)	Endo	6.4	5.2	2 H ₂ O (crystallisation water)	
	II	383–593	519 (515, 537)	Endo	30.6	31.8	2 H ₂ O, 0.71 L fragments of two quinoxaline rings	
	III	593–863	629 (636)	Exo	19.5	20.1	0.58 L next parts of ligands	
	IV	863–1093	808, 838 (744, 757)	Exo	17.8	17.9	0.54 L fragments of ligands containing donor atoms	
				Σ	74.3	75.0		
[Cd(L ²) ₂] _n					25.7	25.0		CdO
	I	623–793	689, 754 (696, 723)	Exo	64.1	63.9	Organic ligands	
[Ca(L ²) ₂ (H ₂ O) ₄]					35.9	36.1		CdO
	I	373–423	390 (393)	Endo	20.1	19.2	4 H ₂ O	
	II	423–743	695 (705)	Exo	22.4	22.2	0.65 L fragments of pyrazine rings	
	III	743–1,083	1021	Exo	29.6	28.8	0.86 L next fragments of rings	
	IV	1083–1273			12.3	12.1	CO ₂	
				Σ	84.4	82.3		
					15.6	17.7		CaO

Thermal analysis of **1**

The thermal stability of **1**, as determined from TG/DTG curves (Fig. 3a) is up to 333 K. **1** loses two uncoordinated water molecules in temperature range 333–383 K. Thermogravimetry shows 5.2% mass loss at such a low temperature which indicates the nature of water molecules,

namely lattice water. The next stage, between 383 and 593 K involves both the loss of two coordinated water molecules and the fragments of two quinoxaline rings. This process is accompanied by endothermic effect (doublet max. 515 and 537 K on DSC curve). The discussed two mass loss steps of the molecules of water (lattice and coordination water) are in good agreement with the crystal



Scheme 3 The structures of the pyrazine-2-carboxylate complexes: **a** $[\text{Cd}(\text{L}^2)_2]_n$ [3], **b** $[\text{Ca}(\text{L}^2)_2(\text{H}_2\text{O})_4]$ [4]

structures of **1** (Fig. 2). The third experimental mass loss of about 21.0% may be attributed to the loss of fragments of pyrazine rings without donor atoms (19.5%). The final step occurs in the temperature range 863–1093 K and represents detachment of donor atoms connected with central ion. Thus, according to X-ray data (Fig. 1), the Cd atom is six-coordinate with two nitrogen atoms of two pyrazine rings and four oxygen atoms, two of carboxylate group of ligands and two of the water molecules, which gives CdN_2O_4 chromophore. At the end of last stage, 25% cadmium oxide remains as final residue, calculated 25.7%. The final solid product was identified on the basis of powder XRD studies [24].

Thermal analysis of 2

A thermal behavior of complex **2** indicates a process with maximum at 693 K which is followed by a single complete decomposition process of sample (Fig. 3b). This process is accompanied by a strong endothermic effect. The experimental mass loss of 63.9% is in good agreement with those calculated of 64.2%. Liu [3] described Cd(II) complex as a two-dimensional coordination polymer in which each central atom is six-coordinated with CdN_2O_4 chromophore (Scheme 3a). The two types of mean lengths bonds: 2.2415 and 2.353 Å support the data from DSC curve (double peaks of 696 and 723 K). The total mass loss occurring up to 793 K is in agreement with the formation of CdO as a final residue (found 36.1, calculated 35.8%). It was confirmed from the XRD patterns [24].

Thermal analysis of 3

The TG curve of **3** shows that the four-stage mass loss occurs in the temperature range of 373–1273 K (Fig. 3c). The first mass loss starts at about 373 K and is about 19.2% and corresponds to the release of all the H_2O molecules (calculated 20.1%). According to X-ray results [4] and Scheme 3b, the complex exists as a monomeric molecule in which the central ion has a distorted dodecahedral

coordination, formed by four water molecules, two nitrogen atoms, and two oxygen atoms from monodentate carboxylic groups of two heterocyclic ligands (Scheme 3b). Taking into consideration that the whole molecules of water in Ca(II) complex are coordination water, the thermal and X-ray data correlated very well. The consecutive stages of the decomposition observed between 423 and 1083 K represents combustion of the pyrazine rings (found 51.0, calculated 51.9%). Further degradation of the previously formed intermediate (CaCO_3) occurs above 1083 K with a weak endothermic effect. On the last step the value of 12.2% calculated for the mass loss is attributed to elimination of carbon dioxide molecule. The mass of the residue obtained corresponds to CaO formation (found 17.7, calculated 15.8%). In addition, the final product was confirmed from XRD patterns [25] and identified on the basis of ICDD using XRAYAN package.

Conclusions

In conclusions, the relationship between the thermal decomposition and structures of metal complexes and the influence of the ligands on thermal behavior of obtained compounds are very important to gain some information about new materials (especially, porous coordination polymers), synthesized by combining organic ligands and metal salts [26–30].

We have successfully synthesized two cadmium and one calcium complexes $[\text{Cd}(\text{L}^1)_2(\text{H}_2\text{O})_2](\text{H}_2\text{O})_2$ (**1**), $[\text{Cd}(\text{L}^2)_2]_n$ (**2**), $[\text{Ca}(\text{L}^2)_2(\text{H}_2\text{O})_4]$ (**3**) via a new, non-hydrothermal reaction and investigated the crystal structure of obtained compounds with X-ray crystallography. By comparing the crystallographic data of **2** and **3**, it can be seen that the crystal structure of the obtained complexes look similar to those reported in the literature [3, 4]. So we concentrated our effort on the spectroscopic data (IR, Raman) and thermal properties of **2** and **3** complexes, and only additionally, on X-ray study for **1**. X-ray structure analysis and IR data confirm that during coordination with Cd(II) 3-hydroxy-2-quinoxalinecarboxylic acid (HL^1) undergoes deprotonation and exists in the keto tautomeric form in complex **1**.

Thermal analysis reveals a decomposition process of **1**, **3** complexes in multiple stages. Data obtained from TG and DSC curve confirm not only the presence but also the nature of water and the stoichiometry of the studied metal complexes. The two mass loss steps of the molecules of water (crystallization and coordination water) are in good agreement with the crystal structures of **1**. A thermal behavior of complex **2** indicates a single complete decomposition process of the sample. In the case of this compound, the two type of mean lengths bonds: 2.2415 and

2.353 Å support the date from DSC curve (double peaks of 696 and 723 K). In addition, complex **2** as a coordination polymer is the most stable and the thermal stability of the obtained complexes can be ordered in the following sequence: **1** < **3** < **2**.

Acknowledgements The authors are grateful to Dr Wiesław Sarga for his help during the thermal work. The opportunity of making an analytical measurement of cadmium ions in the Environmental Analytical Laboratory and the Raman spectra in the Structural Laboratory of the Jan Kochanowski University are also gratefully acknowledged.

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

1. Barszcz B, Hodorowicz M, Jabłońska-Wawrzycka A, Masternak J, Nitek W, Stadnicka K. Comparative study on Cd(II) and Ca(II) model complexes with pyridine-2,3-dicarboxylic acid. Synthesis, crystal structure and spectroscopic investigation. *Polyhedron*. 2010;29:1191–200.
2. Barszcz B, Masternak J, Sarga W. Thermal properties of Ca(II) and Cd(II) complexes of pyridinedicarboxylates. Correlation with crystal structures. *J Therm Anal Calorim*. 2010;101:633–9.
3. Liu G. Poly[bis(2-pyrazine-2-carboxylato)-³N¹,O¹:³N¹,O¹:cadmium(II)]. *Acta Cryst*. 2010;Sect. E66:m93.
4. Ptasiiewicz-Bąk H, Ostrowski A, Leciejewicz J. Monomeric molecules in the isostructural calcium(II) and strontium(II) complexes with pyrazine-2-carboxylic acid. *Polish J Chem*. 1998;72:2014–23.
5. Cevik S, Şaşmaz B, Poyraz M, Sari S, Büyükgüngör O. Synthesis and characterization of Cis-[V^{IV}O(pzc)₂(H₂O)]·2H₂O (pzc: 2-pyrazinecarboxylate). *J Chem Cryst*. 2011;41:796–800.
6. Szorcik A, Nagy L, Scopelliti M, Deák A, Pellerito L, Galbács G, Hered M. Preparation and structural characterization of [Ph₃Sn(IV)]⁺ complexes with pyridine-carboxylic acids or dihydroxypyridine, -pyrimidine and -quinoline. *J Organomet Chem*. 2006;691:1622–30.
7. Goher MAS, Mautner FA, Vicente R. 2D Cu(I) and 3D mixed-valence Cu(I)/Cu(II) coordination polymers: synthesis and structural characterization of [CuCl(pyz-H)₂]:2H₂O and [Cu₂Cl₂(pyz)(H₂O)]·H₂O (pyz-H = pyrazinic acid). *J Mol Struct*. 2007;846:28–33.
8. Premkumar T, Govindarajan S. Transition metal complexes of pyrazinecarboxylic acid with neutral hydrazine as a ligand. Synthesis, spectroscopic, thermal and XRD studies. *J Therm Anal Calorim*. 2005;79:115–21.
9. Erez U, Frenk H, Goldberg O, Kohen A, Teichberg VI. Anti-convulsant properties of 3-hydroxy-2-quinolinecarboxylic acid, a newly found antagonist of excitatory amino acids. *Eur J Pharm*. 1985;110:31–9.
10. Zhang H, Deng J-Y, Bi L-J, Zhou Y-F, Zhang Z-P, Zhang Ch-G, Zhang Y, Zhang X-E. Characterization of *Mycobacterium tuberculosis* nicotinamidase/pyrazinamidase. *FEBS J*. 2008;275:753–62.
11. Premkumar T, Govindarajan S. Antimicrobial study on trivalent lighter rare-earth complexes of pyrazinecarboxylate with hydrazinium cation. *World J Microbiol Biotechnol*. 2006;22:1105–8.
12. Dang Y. Coordination chemistry of cyclopentadienyl titanium carboxylates and related complexes. *Coord Chem Rev*. 1994;135–136:93–128.
13. Olczak-Kobza M, Mrozek A. Zinc(II) and cadmium(II) complexes with *O*-hydroxybenzoic acid or *O*-aminobenzoic acid and 2-methylimidazole. IR spectra, X-ray diffraction studies and thermal analysis. *J Therm Anal Calorim*. 2009;96:555.
14. Vagrová Z, Zeleňák V, Cisařová, Győryová K. Correlation of thermal and spectral properties of zinc(II) complexes of pyridinecarboxylic acids with their crystal structures. *Therm Acta*. 2004;423:149–57.
15. Nonius COLLECT. Delft, The Netherlands: Nonius BV; 1997–2000.
16. Otwinowski Z, Minor W. Processing of X-ray diffraction data collected in oscillation mode. *Methods Enzymol*. 1997;276:307–26.
17. Altomare A, Casarano G, Giacovazzo C, Guagliardi C, Burla MC, Palidori G, Camalli G. *SIR92*—a program for automatic solution of crystal structures by direct methods. *J Appl Cryst*. 1994;27:435–6.
18. Scheldrick GM. *SHELIX-97*, program for crystal structure refinement. Göttingen: University of Göttingen; 1997.
19. Brandenburg K, Putz H. Diamond-crystal and molecular structure visualization crystal impact. Rathausgasse 30, Bonn: GbR. 1997–2000; version 3.2g.
20. Allen FH. *Acta Cryst Sect B*. 2002;58:380–8.
21. Kolev T. Vibrational assignment of in- and out-of-plane modes of some aromatic and arylaliphatic ketones. *J Mol Struct*. 1995;349:381–4.
22. Deacon GB, Phillips RJ. Relationships between the carbon-oxygen stretching frequencies of carboxylate complexes and the type of carboxylate coordination. *Coord Chem Rev*. 1980;33:227–50.
23. Robert V, Lemerrier G. A combined experimental and theoretical study of carboxylate coordination modes: a structural probe. *J Am Chem Soc*. 2006;128:1183–7.
24. Powder diffraction file, JCPDS: ICDD, 1601 Park Lane, Swarthmore, PA 19081, File no. 5–640.
25. Powder diffraction file, JCPDS: ICDD, 1601 Park Lane, Swarthmore, PA 19081, File no. 4–777.
26. Premkumar T, Govindarajan S. Thermoanalytical and spectral properties of new rare-earth metal 2-pyrazinecarboxylate hydrates. *J Therm Anal Calorim*. 2005;79:685–9.
27. Toma HE, Ykeuti AM. Thermoanalytical investigation of the synthesis of pyrazine and bipyrazine via the pyrolysis of the bis(pyrazinecarboxylate)copper(II) complex. *J Therm Anal Calorim*. 1995;45:1331–7.
28. Rzączyńska Z, Kula A, Sienkiewicz-Gromiuk J, Szybiak A. Synthesis, spectroscopic and thermal studies of 2,3-naphthalenedicarboxylates of rare earth elements. *J Therm Anal Calorim*. 2011;103:275–8.
29. Łyszczek R, Iwan M. Investigation of desolvation process in lanthanide dinicotinates. *J Therm Anal Calorim*. 2011;103:633–9.
30. Rzączyńska Z, Danczowska-Burdon A, Sienkiewicz-Gromiuk J. Thermal and spectroscopic properties of light lanthanides(III) and sodium complexes of 2,5-pyridinedicarboxylic acid. *J Therm Anal Calorim*. 2010;101:671–7.